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METHANE SPECTRAL ANALYSIS,

G. Dresselhaus

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Massachusetts Institute of Technology
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20. ABSTRACT *(Continue on reverse side If necessary and identify by block number)*

The vibration-rotation hamiltonian for cubic symmetry molecules was developed using an expansion in terms of angular momentum matrices. A computer program for ground state of the methane molecule was written which gave symmetries and values for the rotational levels. A perturbation theory was developed for the excited vibrational states based on a spherical jellium molecule for the ground state. This perturbation was shown to give good convergence for the nearly degenerate ν_2, ν_4 vibrational levels in methane. Preliminary work on the develop-

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ment of computer programs for a calculation of the vibrational levels of molecules using LCAO X_α calculations for the electronic structure was carried out.

Accomplishments

The main accomplishments of the research carried out under this contract are discussed in this section. The first year was devoted to computer coding the rotational Hamiltonians for the various vibrational states in methane. The second and third years were devoted to a new formulation of the model Hamiltonian based on a jellium approximation for the molecule. Finally, in the third year, consideration was given to a calculation of the vibrational modes of simple molecules based on the electronic structure of these molecules. This latter work is continuing under AFOSR grant #77-3130.

The calculation of the rotational levels of the high symmetry molecules was carried out using standard techniques developed for simpler low symmetry molecules. The computer code was written with the help of Samuel Safran who finished a Ph.D. degree at M.I.T. and then obtained a position at Bell Laboratories. It was shown that the Wang representation for the angular momentum matrices gives rise to a factorization of the rotational Hamiltonian for $\underline{all}$ symmetrices of vibrational states. This general result is applied to the methane molecule below.

The molecular vibration rotation energy levels for the methane molecule are formulated making full use of the high symmetry of this molecule. The vibration-rotation Hamiltonian in Td symmetry obtained by the angular momentum matrix expansion. The use of the Wang representation of the $[3 \times (2J + 1)]$ dimensioned matrices for the F_2 symmetry (ν_3 or ν_4) levels into four blocks. In this fractorization, three of the four blocks have identical eigenvalue and are associated with F_1 and F_2 symmetry rotational levels whereas the remaining block contains states of A_1, A_2 and E symmetry.

The block form of the rotational Hamiltonian coupling ν_1 and ν_4 vibrational levels is given by:

$$
\begin{array}{c}
\tilde{\nu}_1 \qquad\qquad\qquad\qquad \overbrace{\qquad\qquad\qquad \nu_4 \qquad\qquad\qquad} \\[1em]
\begin{array}{cc|cccccccccc}
I_{oo} & 0 & & & 0 & I_x & & I_y & 0 & 0 & I_z & \\
0 & II_{oo} & & & II_x & 0 & & 0 & II_y & I_z^+ & 0 & \\
& & III_{oo} & 0 & 0 & II_x^+ & & I_y^+ & 0 & & & 0 & II_z \\
& & 0 & IV_{oo} & I_x^+ & 0 & & 0 & II_y^+ & & & II_z^+ & 0 \\
\hline
& & & I_{xx} & 0 & & 0 & I_z & & & I_y & 0 \\
& & & 0 & II_{xx} & & I_z^+ & 0 & & & 0 & II_y \\
& & & & III_{xx} & 0 & & 0 & II_z & I_y^+ & 0 \\
& & & & 0 & IV_{xx} & & II_z^+ & 0 & 0 & II_y^+ \\
& & & & & & I_{yy} & 0 & & & 0 & I_x \\
& & & & & & 0 & II_{yy} & & & II_x & 0 \\
& & & & & & & III_{yy} & 0 & 0 & II_x^+ \\
& & & & & & & 0 & IV_{yy} & I_x^+ & 0 \\
& & & & & & & & & I_{zz} & 0 \\
& & & & & & & & & 0 & II_{zz} \\
& & & & & & & & & & III_{zz} & 0 \\
& & & & & & & & & & 0 & IV_{zz} \\
\end{array}
\end{array}
$$

The numerical results for the ground state of the methane molecule are given in Appendix A. It was found that angular momentum values up to $J \approx 40$ could be solved with modest amounts of computer time.

The jellium model for high symmetry molecules was developed in order to simplify the calculation of the coupled vibrations-rotation Hamiltonian. This simplification is both in terms of limiting the number of parameters for the Hamiltonian and in the diagonalization of the resulting matrix. These questions together with a complete exposition of the model are the subject of a paper which is included as Appendix B. This paper was submitted to the Journal of Molecular Spectroscopy.

Finally, during the final few months of this contract, consideration was given to a calculation of the vibrational frequencies of the methane molecule. A force constant model for methane was developed and the evaluation of the force constants based on the electronic structure was considered. Our electronic state calculations are carried out using scattered wave X_α programs developed at MIT. This work was carried out in collaboration with Miss Iris Howard who is the holder of an IBM Graduate Fellowship. Work is continuing on this project under an AFOSR grant.

Appendix A. Ground State Rotational Levels for Methane

The rotational Hamiltonian for the methane molecule with T_d symmetry is diagonalized in a fortran program which is available on request. The program uses as inputs the coefficients of the terms in the Hamiltonian and computes the eigenvalues for various values of angular momentum, J. The symmetry of the eigenvector is also determined.

The program makes use of the Wang transformation on the angular momentum matrices of the rotational Hamiltonian into four blocks. Because of the symmetry imposed degeneracies, only two of these blocks need to be diagonalized.

The output from this computer program for the ground state of the methane molecule is given below.

A1000A,A1002A,A1004A,A1005A,A1008A,A10010A,A10012A
0. -265677.1702 796749.568437 63.7867435 0. 0. 0.
 A1004B,A1006B,A1008B,A10010B,A10012B
-1328082.4105 -409.7844325 0. 0. 0.
 A1006C,A1008C,A10010C,A10012C
424.8167 0. 0. 0.
 A1008D,A10010D,A10012D
0. 0. 0.
 A10010E,A10012E
0. 0.
 A10012F
0.

        BAND CENTER FOR NUO=   0.00000 A1 SYMMETRY   J=0

    J= 1   -.1020340   F1 SYMMETRY

    2
    J= 2   -.478230514E+07   E   X(S4)=   .000
    J= 2   .318819707E+07   F2   X(S4)= -1.000

    3
    J= 3   .796883601E+07   F2   X(S4)= -1.000
    J= 3   -.238957147E+08   F1   X(S4)= 1.000
    J= 3   .477804077E+08   A2   X(S4)= -1.000

    4
    J= 4   -.158570692E+08   E   X(S4)=   .000
    J= 4   -.111457354E+07   A1   X(S4)= 1.000
    J= 4   .103413889E+07   F2   X(S4)= -1.000
    J= 4   -.556905222E+08   F1   X(S4)= 1.000

    5
    J= 5   .218478781E+09   F1   X(S4)= 1.000
    J= 5   -.111037280E+09   F2   X(S4)= -1.000
    J= 5   -.218632775E+09   F1   X(S4)= 1.000
    J= 5   .166783976E+09   E   X(S4)= 0.000

    6
    J= 6   .499916884E+09   A1   X(S4)= 1.000
    J= 6   -.260902158E+09   A2   X(S4)= -1.000
    J= 6   -.452483325E+09   E   X(S4)=   .000
    J= 6   .380866360E+09   F1   X(S4)= 1.000
    J= 6   .246071404E+09   F2   X(S4)= -1.000
    J= 6   -.404960635E+09   F2   X(S4)= 1.000

    7
    J= 7   .814136603E+09   F1   X(S4)= 1.000
    J= 7   .391116452E+09   F2   X(S4)= -1.000
    J= 7   -.748611890E+09   F2   X(S4)= 1.000
    J= 7   -.855388314E+09   F1   X(S4)= 1.000
    J= 7   .557998597E+09   E   X(S4)=   .000
    J= 7   .801919779E+08   A2   X(S4)= -1.000

J= 8	-.11239146E+10	E	X(S4)=	.000
J= 8	-.13934740E+10	E	X(S4)=	-.000
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J= 8	.132315055E+10	F2	X(S4)=	-1.000
J= 8	.678721404E+09	F1	X(S4)=	1.000
J= 8	.112113836E+09	F2	X(S4)=	-1.000
J= 8	-.145124955E+10	F1	X(S4)=	1.000

9

J= 9	.196640716E+10	F2	X(S4)=	-1.000
J= 9	.166490114E+10	F1	X(S4)=	1.000
J= 9	.174322030E+09	F1	X(S4)=	1.000
J= 9	-.237160764E+10	F2	X(S4)=	-1.000
J= 9	-.247308927E+10	F1	X(S4)=	1.000
J= 9	.220200506E+10	A2	X(S4)=	-1.000
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J=10	-.300196470E+09	F2	X(S4)=	-1.000
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11

J=11	.453514987E+10	F1	X(S4)=	1.000
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J=11	-.570519565E+10	F2	X(S4)=	-1.000
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J=13	.222430205E+10	F1	X(S4)=	1.000
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22 (~100 sec)

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J=22	.561322973E+10	F2	X(S4)=	-1.000
J=22	-.197176933E+11	F1	X(S4)	1.000
J=22	-.553050602E+11	F1	X(S4)=	1.000
J=22	-.553668299E+11	F2	X(S4)=	-1.000
J=22	-.100443847E+12	F2	X(S4)=	-1.000

23 (121 sec)

J=23	.840996073E+11	F1	X(S4)= 1.000
J=23	.833176634E+11	F2	X(S4)= -1.000
J=23	.533207802E+11	F1	X(S4)= 1.000
J=23	.475905054E+11	F2	X(S4)= -1.000
J=23	.286420425E+11	F2	X(S4)= -1.000
J=23	.244654390E+11	F1	X(S4)= 1.000
J=23	.413649765E+10	F1	X(S4)= 1.000
J=23	-.270305703E+11	F2	X(S4)= -1.000
J=23	-.274902905E+11	F1	X(S4)= 1.000
J=23	-.684216956E+11	F2	X(S4)= -1.000
J=23	-.119866075E+12	F2	X(S4)= -1.000
J=23	-.119868010E+12	F1	X(S4)= 1.000
J=23	.837273503E+11	E	X(S4)= .000
J=23	.503072350E+11	E	X(S4)= .000
J=23	.354030204E+11	A2	X(S4)= 1.000
J=23	.682332081E+10	A1	X(S4)= 1.000
J=23	.306103781E+10	E	X(S4)= .000
J=23	-.683987121E+11	E	X(S4)= .000
J=23	-.684674733E+11	A2	X(S4)= -1.000

24 (145 sec)

J=24	.998059556E+11	A1	X(S4)= 1.000
J=24	.987483172E+11	A2	X(S4)= -1.000
J=24	.616429920E+11	E	X(S4)= .000
J=24	.301460175E+11	E	X(S4)= .000
J=24	.220663626E+11	A1	X(S4)= 1.000
J=24	-.360115953E+11	A2	X(S4)= -1.000
J=24	-.365500093E+11	E	X(S4)= .000
J=24	-.141838074E+12	E	X(S4)= .000
J=24	-.141840127E+12	A1	X(S4)= 1.000
J=24	.794701234E+11	F1	X(S4)= 1.000
J=24	.991182678E+11	F2	X(S4)= -1.000
J=24	.637118708E+11	F2	X(S4)= -1.000
J=24	.577657832E+11	F1	X(S4)= 1.000
J=24	.409198594E+11	F2	X(S4)= -1.000
J=24	.271027010E+11	F1	X(S4)= 1.000
J=24	.128053854E+10	F1	X(S4)= 1.000
J=24	-.626606366E+09	F2	X(S4)= -1.000
J=24	-.363792060E+11	F2	X(S4)= -1.000
J=24	-.835397360E+11	F1	X(S4)= 1.000
J=24	-.835738952E+11	F2	X(S4)= -1.000
J=24	-.141838758E+12	F1	X(S4)= 1.000

25 (160 sec)

J=25	.117210179E+12	F1	X(S4)=	1.000
J=25	.116582049E+12	F2	X(S4)=	-1.000
J=25	.746761122E+11	F2	X(S4)=	-1.000
J=25	.719535120E+11	F1	X(S4)=	1.000
J=25	.481866043E+11	F1	X(S4)=	1.000
J=25	.302761000E+11	F2	X(S4)=	-1.000
J=25	.237143473E+11	F1	X(S4)=	1.000
J=25	-.484035867E+10	F2	X(S4)=	-1.000
J=25	-.470876344E+11	F2	X(S4)=	-1.000
J=25	-.473694162E+11	F1	X(S4)=	1.000
J=25	-.100912746E+12	F1	X(S4)=	1.000
J=25	-.166533072E+12	F2	X(S4)=	-1.000
J=25	-.166534038E+12	F1	X(S4)=	1.000
J=25	.116898697E+12	E	X(S4)=	.000
J=25	.769273615E+11	A2	X(S4)=	-1.000
J=25	.680700680E+11	A1	X(S4)=	1.000
J=25	.450195747E+11	E	X(S4)=	.000
J=25	-.395389360E+10	E	X(S4)=	-.000
J=25	-.643433399E+10	A2	X(S4)=	-1.000
J=25	-.100887448E+12	A1	X(S4)=	1.000
J=25	-.100925372E+12	E	X(S4)=	.000

26 (180 sec)

J=26	.136693673E+12	E	X(S4)=	.000
J=26	.869231185E+11	E	X(S4)=	.000
J=26	.615893310E+11	A1	X(S4)=	1.000
J=26	.318694875E+11	A2	X(S4)=	-1.000
J=26	.229526262E+11	E	X(S4)=	-.000
J=26	-.598697665E+11	E	X(S4)=	.000
J=26	-.601986533E+11	A1	X(S4)=	1.000
J=26	-.194122343E+12	A2	X(S4)=	-1.000
J=26	-.194123365E+12	E	X(S4)=	-.000
J=26	.136964476E+12	F2	X(S4)=	-1.000
J=26	.136409442E+12	F1	X(S4)=	1.000
J=26	.896280914E+11	F2	X(S4)=	-1.000
J=26	.842536831E+11	F1	X(S4)=	1.000
J=26	.549834839E+11	F1	X(S4)=	1.000
J=26	.491672472E+11	F2	X(S4)=	-1.000
J=26	.252139081E+11	F2	X(S4)=	-1.000
J=26	-.106408363E+11	F1	X(S4)=	1.000
J=26	-.121108064E+11	F2	X(S4)=	-1.000
J=26	-.599803936E+11	F1	X(S4)=	1.000
J=26	-.120650797E+12	F1	X(S4)=	1.000
J=26	-.120669420E+12	F2	X(S4)=	-1.000
J=26	-.194123024E+12	F2	X(S4)=	-1.000

27 $\quad$ 212 oer

J=27	.158945863E+12	F2	X(S4)= -1.000
J=27	.158703063E+12	F1	X(S4)= 1.000
J=27	.105019773E+12	F1	X(S4)= 1.000
J=27	.998283411E+11	F2	X(S4)= -1.000
J=27	.703032320E+11	F1	X(S4)= 1.000
J=27	.551638128E+11	F2	X(S4)= -1.000
J=27	.252309636E+11	F2	X(S4)= -1.000
J=27	.210485661E+11	F1	X(S4)= 1.000
J=27	-.195466939E+11	F1	X(S4)= 1.000
J=27	-.747139330E+11	F2	X(S4)= -1.000
J=27	-.748844771E+11	F1	X(S4)= 1.000
J=27	-.142967940E+12	F2	X(S4)= -1.000
J=27	-.224774191E+12	F2	X(S4)= -1.000
J=27	-.224774671E+12	F1	X(S4)= 1.000
J=27	.159182885E+12	A2	X(S4)= -1.000
J=27	.158454120E+12	A1	X(S4)= 1.000
J=27	.102934327E+12	E	X(S4)= .000
J=27	.600728722E+11	E	X(S4)= .000
J=27	.455886575E+11	A2	X(S4)= -1.000
J=27	-.183100578E+11	A1	X(S4)= 1.000
J=27	-.201244495E+11	E	X(S4)= .000
J=27	-.142961092E+12	E	X(S4)= .000
J=27	-.142981624E+12	A2	X(S4)= -1.000

28

J=28	.183459924E+12	E	X(S4)= -.000
J=28	.123488437E+12	A1	X(S4)= 1.000
J=28	.116145010E+12	A2	X(S4)= -1.000
J=28	.774311401E+11	E	X(S4)= -.000
J=28	.216997175E+11	E	X(S4)= .000
J=28	.157594810E+11	A1	X(S4)= 1.000
J=28	-.917224137E+11	A2	X(S4)= -1.000
J=28	-.919189882E+11	E	X(S4)= -.000
J=28	-.258649117E+12	E	X(S4)= .000
J=28	-.258649625E+12	A1	X(S4)= 1.000
J=28	.183669610E+12	F2	X(S4)= -1.000
J=28	.183248387E+12	F1	X(S4)= 1.000
J=28	.121437330E+12	F1	X(S4)= 1.000-
J=28	.119065622E+12	F2	X(S4)= -1.000
J=28	.816086879E+11	F2	X(S4)= -1.000
J=28	.634764506E+11	F1	X(S4)= 1.000
J=28	.501709317E+11	F2	X(S4)= -1.000
J=28	.194926605E+11	F1	X(S4)= 1.000
J=28	-.289688901E+11	F1	X(S4)= 1.000
J=28	-.299197618E+11	F2	X(S4)= -1.000
J=28	-.918537566E+11	F2	X(S4)= -1.000
J=28	-.167997234E+12	F1	X(S4)= 1.000
J=28	-.168007279E+12	F2	X(S4)= -1.000
J=28	-.258649286E+12	F1	X(S4)= 1.000

29

J=29	.210938993E+12	F1	X(S4)=	1.000
J=29	.210576875E+12	F2	X(S4)=	-1.000
J=29	.142050394E+12	F1	X(S4)=	1.000
J=29	.137622947E+12	F2	X(S4)=	-1.000
J=29	.924343447E+11	F2	X(S4)=	-1.000
J=29	.854456272E+11	F1	X(S4)=	1.000
J=29	.557060825E+11	F1	X(S4)=	1.000
J=29	.165349770E+11	F2	X(S4)=	-1.000
J=29	.126303724E+11	F1	X(S4)=	1.000
J=29	-.412803006E+11	F2	X(S4)=	-1.000
J=29	-.111258720E+12	F2	X(S4)=	-1.000
J=29	-.111358642E+12	F1	X(S4)=	1.000
J=29	-.195924748E+12	F1	X(S4)=	1.000
J=29	-.295901754E+12	F2	X(S4)=	-1.000
J=29	-.295901994E+12	F1	X(S4)=	1.000
J=29	.210760046E+12	E	X(S4)=	0.000
J=29	.139852453E+12	E	X(S4)=	0.000
J=29	.988832272E+11	A2	X(S4)=	-1.000
J=29	.701023553E+11	A1	X(S4)=	1.000
J=29	.517816642E+11	E	X(S4)=	.000
J=29	-.408863112E+11	E	X(S4)=	-.000
J=29	-.420413109E+11	A2	X(S4)=	-1.000
J=29	-.195917388E+12	A1	X(S4)=	1.000
J=29	-.195928427E+12	E	X(S4)=	.000

30

J=30	.241112892E+12	A1	X(S4)=	1.000
J=30	.240649985E+12	A2	X(S4)=	-1.000
J=30	.161961379E+12	E	X(S4)=	-.000
J=30	.102466796E+12	E	X(S4)=	-.000
J=30	.782752973E+11	A1	X(S4)=	1.000
J=30	.113284208E+11	A2	X(S4)=	-1.000
J=30	.637098195E+10	E	X(S4)=	-.000
J=30	-.133288986E+12	E	X(S4)=	.000
J=30	-.133403251E+12	A1	X(S4)=	1.000
J=30	-.336677546E+12	A2	X(S4)=	-1.000
J=30	-.336677800E+12	E	X(S4)=	-.000
J=30	.240960407E+12	F1	X(S4)=	1.000
J=30	.240806122E+12	F2	X(S4)=	-1.000
J=30	.163758668E+12	F2	X(S4)=	-1.000
J=30	.159694938E+12	F1	X(S4)=	1.000
J=30	.111723525E+12	F2	X(S4)=	-1.000
J=30	.960055657E+11	F1	X(S4)=	1.000
J=30	.597135576E+11	F1	X(S4)=	1.000
J=30	.523247744E+11	F2	X(S4)=	-1.000
J=30	.787213564E+10	F2	X(S4)=	-1.000
J=30	-.548803618E+11	F1	X(S4)=	1.000
J=30	-.555070749E+11	F2	X(S4)=	-1.000
J=30	-.133327157E+12	F1	X(S4)=	1.000
J=30	-.226888627E+12	F1	X(S4)=	1.000
J=30	-.226894015E+12	F2	X(S4)=	-1.000
J=30	-.336677715E+12	F2	X(S4)=	-1.000

```
31
J=31        .274125249E+12      F1      X(S4)=    1.000
J=31        .273864533E+12      F2      X(S4)=   -1.000
J=31        .187003401E+12      F2      X(S4)=   -1.000
J=31        .185271158E+12      F1      X(S4)=    1.000
J=31        .128022405E+12      F1      X(S4)=    1.000
J=31        .110945865E+12      F2      X(S4)=   -1.000
J=31        .862753010E+11      F1      X(S4)=    1.000
J=31        .544452934E+11      F2      X(S4)=   -1.000
J=31        .814919915E+07      F2      X(S4)=   -1.000
J=31       -.176646893E+10      F1      X(S4)=    1.000
J=31       -.713671256E+11      F1      X(S4)=    1.000
J=31       -.158033336E+12      F2      X(S4)=   -1.000
J=31       -.158096367E+12      F1      X(S4)=    1.000
J=31       -.261050628E+12      F2      X(S4)=   -1.000
J=31       -.381111916E+12      F2      X(S4)=   -1.000
J=31       -.381112037E+12      F1      X(S4)=    1.000
J=31        .273995177E+12      E       X(S4)=     .000
J=31        .188742531E+12      A2      X(S4)=   -1.000
J=31        .183233073E+12      A1      X(S4)=    1.000
J=31        .123060772E+12      E       X(S4)=     .000
J=31        .590182304E+11      E       X(S4)=    -.000
J=31        .469524709E+11      A2      X(S4)=   -1.000
J=31       -.708632910E+11      A1      X(S4)=    1.000
J=31       -.716142332E+11      E       X(S4)=     .000
J=31       -.261048654E+12      E       X(S4)=    -.000
J=31       -.261054575E+12      A2      X(S4)=   -1.000


32
J=32        .310258074E+12      E       X(S4)=    -.000
J=32        .213033656E+12      E       X(S4)=     .000
J=32        .150095024E+12      A1      X(S4)=    1.000
J=32        .124396393E+12      A2      X(S4)=   -1.000
J=32        .907644994E+11      E       X(S4)=    -.000
J=32       -.971900490E+10      E       X(S4)=     .000
J=32       -.130047120E+11      A1      X(S4)=    1.000
J=32       -.185638046E+12      A2      X(S4)=   -1.000
J=32       -.185704157E+12      E       X(S4)=    -.000
J=32       -.429327779E+12      E       X(S4)=     .000
J=32       -.429327908E+12      A1      X(S4)=    1.000
J=32        .310366690E+12      F2      X(S4)=   -1.000
J=32        .310140287E+12      F1      X(S4)=    1.000
J=32        .214645209E+12      F2      X(S4)=   -1.000
J=32        .211395606E+12      F1      X(S4)=    1.000
J=32        .143956755E+12      F1      X(S4)=    1.000
J=32        .136689154E+12      F2      X(S4)=   -1.000
J=32        .965820569E+11      F2      X(S4)=   -1.000
J=32        .561806079E+11      F1      X(S4)=    1.000
J=32        .473417900E+11      F2      X(S4)=   -1.000
J=32       -.100868574E+11      F1      X(S4)=    1.000
J=32       -.897533057E+11      F1      X(S4)=    1.000
J=32       -.901461905E+11      F2      X(S4)=   -1.000
J=32       -.185682143E+12      F2      X(S4)=   -1.000
J=32       -.298541079E+12      F1      X(S4)=    1.000
J=32       -.298543974E+12      F2      X(S4)=   -1.000
J=32       -.429327822E+12      F1      X(S4)=    1.000
```

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33
J=33          .349878456E+12      F2     X(S4)=  -1.000
J=33          .349787757E+12      F1     X(S4)=   1.000
J=33          .244017566E+12      F1     X(S4)=   1.000
J=33          .241149855E+12      F2     X(S4)=  -1.000
J=33          .168279504E+12      F1     X(S4)=   1.000
J=33          .153467932E+12      F2     X(S4)=  -1.000
J=33          .105244540E+12      F2     X(S4)=  -1.000
J=33          .945059033E+11      F1     X(S4)=   1.000
J=33          .466608532E+11      F1     X(S4)=   1.000
J=33         -.223806800E+11      F2     X(S4)=  -1.000
J=33         -.242820855E+11      F1     X(S4)=   1.000
J=33         -.111105544E+12      F2     X(S4)=  -1.000
J=33         -.216300305E+12      F2     X(S4)=  -1.000
J=33         -.216333729E+12      F1     X(S4)=   1.000
J=33         -.339496483E+12      F1     X(S4)=   1.000
J=33         -.481434681E+12      F2     X(S4)=  -1.000
J=33         -.481434742E+12      F1     X(S4)=   1.000
J=33          .349968666E+12      A2     X(S4)=  -1.000
J=33          .349696563E+12      A1     X(S4)=   1.000
J=33          .242673037E+12      E      X(S4)=    .000
J=33          .160365079E+12      E      X(S4)=   -.000
J=33          .121552902E+12      A2     X(S4)=  -1.000
J=33          .551021287E+11      A1     X(S4)=   1.000
J=33          .434158289E+11      E      X(S4)=    .000
J=33         -.110949334E+12      E      X(S4)=   -.000
J=33         -.111414828E+12      A2     X(S4)=  -1.000
J=33         -.339494357E+12      A1     X(S4)=   1.000
J=33         -.339497546E+12      E      X(S4)=    .000
```

Appendix B.   <u>Jellium Model</u>

The jellium model is developed theoretically in the preprint which is included below. A computer program based on this model was also written. However, the program used to test the model for the coupled v_2, v_4 bands in methane, as well as the experimental data set used to determine the goodness of fit was that of Professor Alan Robiettle of the Department of Chemistry, Reading University, Reading, England.

PHENOMENOLOGICAL MOLECULAR

ROTATIONAL HAMILTONIANS IN CUBIC SYMMETRY

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28 pages

0 figures

6 tables

Running Title: Phenomenological...Hamiltonians

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Abstract

Group theoretical techniques are employed to derive the form of the most general phenomenological rotational Hamiltonian associated with a given molecular vibrational state or set of states. The expansion is given in terms of the symmetrized products of angular momentum matrices. A perturbation expansion for the rotational states is developed based on tetrahedral distortions of a spherically symmetric distribution of mass. This jellium approximation significantly reduces the number of parameters in the rotational Hamiltonian. The specific application to methane is indicated.

I. Introduction

Phenomenological Hamiltonians are widely used in physics to model physical systems. Their introduction is motivated by either (1) an attempt to model an extremely complex many-particle system by a simple one-particle mathematical formulation or (2) the necessity of refining theoretical models to fit a multitude of precise experimental data. An example of the first point is the introduction of pseudopotentials in the theory of the electronic structure of solids,[1] whereas an example of the second is the use of phenomenological rotational Hamiltonians to fit the IR and Raman spectra of molecules.[2]

The development of these Hamiltonians has traditionally made extensive use of symmetry in determining the functional form. The high symmetry molecules require extensive use of group theory for the primary reason that symmetry imposes mode degeneracies which must be explicitly included in order to successfully model the vibrational and rotational states. The extensively studied molecule with T_d symmetry, CH_4,[3] will be explicitly considered in this paper. However the higher symmetry molecules with O_h symmetry, e.g. SF_6 or UF_6 can be treated by exactly the same formalism as that developed here.

The methane molecule has 4 distinct vibrational frequencies labelled by v_1, v_2, v_3 and v_4, corresponding to the 9 degrees of vibrational motion,[2] which consist of one non-degenerate v_1 mode with A_1 symmetry, two degenerate v_2 modes with E symmetry and two three-fold v_3 and v_4 modes with F_2 symmetry. In addition to these symmetry-imposed degeneracies (which require special consideration in the derivation of the phenomenological Hamiltonian), there are near-degeneracies that are accidental. Two examples of such near-degeneracies in methane are: (1) v_2 and v_4, and (2) v_1, v_3 the overtones $(2v_2)$ and $(2v_4)$ and the combination modes $(v_2 + v_4)$. The fitting of the vibronic modes in CH_4 is greatly perturbed by the interactions between the levels of these degenerate and nearly degenerate states.

This paper addresses the formulation of the phenomenological Hamiltonian for the rotational-vibrational states in a high symmetry molecule and develops a perturbation expansion based on deviations from spherical symmetry. This formulation makes it possible to treat a collection of degenerate and nearly degenerate levels using the minimal number of terms required by symmetry considerations in the phenomenological Hamiltonian. Using the functional form based on group theoretical considerations, the coefficients of the model Hamiltonians can be evaluated by comparison with experiment. Though application is made to CH_4 having modes with A_1, E and $2F_2$ symmetries, the same formulation is easily extended to other molecules with T_d symmetry, such as $Ni(CO)_4$ having modes with $2A_1$, 2E, F_1 and $4F_2$ symmetries. The extension to high symmetry molecules with different cubic symmetries can also be carried out based on the functional form presented in this paper.

The general symmetry considerations which apply to all phenomenological Hamiltonians are discussed in Section II and these principles are applied to vibrational-rotational Hamiltonians for T_d symmetry molecules. Section III develops a perturbation expansion based on the spherically symmetric phenomenological Hamiltonian for "jellium" which allows one to greatly reduce the number of expansion coefficients. Section IV makes the application of the perturbed jellium model to the methane molecule and finally Section V gives a brief summary of the current paper.

II. General Theoretical Development

A phenomenological Hamiltonian $\mathcal{H}_{\Gamma_1}(\theta_1, \theta_2, \ldots \theta_n)$ in general depends on the operators θ_i and is a scalar with respect to the symmetry operations of the symmetry group of the system. Thus if R is any symmetry operation (including time inversion), that leaves the Hamlitonian invariant; then

$$R \, \mathcal{H}_{\Gamma_1}(\theta_1, \theta_2, \ldots \theta_n) = \mathcal{H}_{\Gamma_1}(\theta_1, \theta_2, \ldots \theta_n). \tag{1}$$

The invariance of $\mathcal{H}_{\Gamma_1}$ under the symmetry operations R does not otherwise restrict the form of $\mathcal{H}_{\Gamma_1}$, so that $\mathcal{H}_{\Gamma_1}$ can be a matrix, which is the case if $\mathcal{H}_{\Gamma_1}$ represents the rotations of a vibrating molecule. The operators θ_i are also not necessarily scalars under the symmetry operations R. These apparent complexities can be systematically handled by elementary group theoretical considerations, and this is the focus of the present paper.

The symmetrized form of $\mathcal{H}_{\Gamma_1}(\theta_1, \theta_2, \ldots \theta_n)$ can be based on the assumption that its functional form is a power series[4] in one or more operators. This assumption is not necessary, but is convenient because a function of an operator $f(\theta)\Psi$ is usually defined in terms of a power series expansion in the operator, i.e. $\{f(0) + f'(0)\theta + \ldots\}\Psi$. From this point of view, the Hamiltonian is written in terms of a complete set of basis matrices $B(\Gamma_i)$ which transform as the irreducible representation Γ_i

$$\mathcal{H}_{\Gamma_1}(\theta_1, \theta_2, \ldots \theta_n) = \Sigma\{B(\Gamma_i), A_{\Gamma_i}(\theta_1, \ldots, \theta_n)\}_{\Gamma_1} \tag{2}$$

where the $A_{\Gamma_i}(\theta_1 \ldots \theta_n)$ are symmetrized polynomial functions of the operators $\theta_1, \theta_2, \ldots \theta_n$ that transform according to the irreducible representation Γ_i. The basis matrices $B(\Gamma_i)$ can be classified according to the irreducible representation of the symmetry group of the molecule and the scalar combination of B and A is taken in Eq. (2). Time reversal symmetry must also be explicitly considered, so that the basis matrices are either even or odd under time reversal.

If a given irreducible representation is n-dimensional, then there are n^2 basis matrices of rank n, of which $n(n-1)/2$ are odd under time reversal and $n(n+1)/2$ are even. The formulation given here is quite general. When applied to the development of phenomenological Hamiltonians for solids, space groups must be used, whereas for molecules point groups are used.

A general expansion for degenerate or nearly-degenerate states (whether vibrational or electronic) is obtained by use of angular momentum matrices,[4] $\vec{L}$. Use of these basis matrices is common for electronic[5] E vs $\vec{k}$ or phonon[6] ω vs $\vec{q}$ in crystals and was first introduced for molecular rotational Hamiltonians by Landau and Lifshitz.[7] The rotational Hamiltonian for the vibrational state characterized by the angular momentum quantum number ℓ taken to order $(2n)$ in the angular momentum matrices $\vec{J}$ is designated by $\mathcal{H}_{\ell\ell}^{(2n)}$ and is given by

$$\mathcal{H}_{\ell\ell}^{(2n)}(\vec{J}) = \sum_{\mu=0}^{2n} \sum_{\lambda=0}^{2\ell,\{\frac{\mu}{2}\}} \sum_{\nu=0}^{} \sum_{\Gamma_i} a_{\Gamma_i}^{(\ell\ell)}(\mu,\lambda,\nu)[j(j+1)]^\nu \{j_{\Gamma_i}^{(\lambda)}(\vec{L}^{(\ell)}), j_{\Gamma_i}^{(\mu-2\nu)}(\vec{J})\}_{A_1}$$

(3)

The parameters of the expansion $a_{\Gamma_i}^{(\ell\ell)}(\mu,\lambda,\nu)$ are indexed according to symmetry type Γ_i and to the three indices μ,λ, and ν, where μ denotes the exponent of angular momentum $\vec{J}, \lambda$ the exponent for angular momentum $\vec{L}^{(\ell)}$, and ν the exponent for the product $(\vec{J} \cdot \vec{J}) = j(j+1)$ where $j(j+1)$ is the eigenvalue of J^2. The symmetrized combinations of angular momentum matrices $j_{\Gamma_i}^{(\lambda')}(\vec{J})$ are labelled according to symmetry type Γ_i and to the order of the basis function λ'. Explicit symmetrized linear combinations corresponding to T_d symmetry are given by Altmann and Cracknell[8] for $0 \leq \lambda' \leq 12$. The curly bracket $\{ , \}_{A_1}$ indicates that symmetrized combinations of $j_{\Gamma_i}^{(\lambda)}(\vec{L}^{(\ell)})$ and $j_{\Gamma_i}^{(\mu-2\nu)}(\vec{J})$ are taken so that a scalar Hamiltonian results and the non-commuting quantum mechanical operators are symmetrized. The prime on the summation over λ denotes the constraint that $\lambda + \mu =$ even and the sum over ν is cut off at the largest integer in $(\mu/2)$.

Further constraints on the summations in Eq. (3) are presented below. These constraints depend on the properties of the symmetrized basis functions $j_{\Gamma_i}^{(\lambda')}(\vec{J})$ which are now discussed.

The symmetrized products of angular momentum matrices $j_{\Gamma_i}^{(\lambda)}(\vec{L}^{(\ell)})$ span the vector space appropriate to angular momentum ℓ and are determined by the dimension of the set of levels. For example, for a non-degenerate level, only one matrix is needed, the unit matrix (1), so that $J_{A_1}^{(0)}(\vec{L}^{(o)}) \equiv (1)$ for $\lambda = 0$. For a 3-fold degenerate level, $\ell = 1$ in Eq. (3) and 9 basis functions are required for span the vector space. These basis functions are found from the direct product of the symmetry type F_1 for $\ell=1$, namely $F_1 \times F_1 = A_1 + F_1 + E + F_2$. These 9 basis functions for T_d symmetry are given by $j_{\Gamma_i}^{(\lambda)}(\vec{L}^{(\ell)})$ where $\ell = 1$ and $\lambda = 0,1,2$. The matrices $\vec{L}^{(1)}$ given by[4]

$$
L_x^{(1)} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & i \\ 0 & -i & 0 \end{pmatrix} , \qquad L_y^{(1)} = \begin{pmatrix} 0 & 0 & -i \\ 0 & 0 & 0 \\ i & 0 & 0 \end{pmatrix} , \qquad L_z^{(1)} = \begin{pmatrix} 0 & i & 0 \\ -i & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \qquad (4)
$$

respectively, generate the 9 basis functions for a 3-fold degenerate level with F_1 symmetry in the T_d group. The normalization is given by

$$
\sum_{\Gamma_i} \{ j_{\Gamma_i}^{(\lambda)}(\vec{J}), \ j_{\Gamma_i}^{(\lambda)}(\vec{J}) \}_{A_1} \equiv (\vec{J} \cdot \vec{J})^\lambda \tag{5}
$$

where the sum is over all the irreducible representations that occur for a given λ, $\vec{J} \cdot \vec{J} = J^2$ and the curly bracket denotes a scalar product of the symmetrized basis functions. For $\lambda \geqslant 5$, multiple occurrences of a given irreducible representation are found, as for example F_1 and F_1, for $\lambda = 5$, and F_2 and F_2, for $\lambda = 6$. Thus, if λ or $(\mu - 2\nu)$ in Eq. (3) exceed 4, then the sum over representations must include multiple occurrences such as F_1 and F_1, for $\lambda = 5$, and F_2 and F_2, for $\lambda = 6$. Similarly if $\ell > 2$ in Eq. (3),

then λ will exceed 4 and multiple occurrences of representations must again by explicitly included. Also note that the functions of $j_{\Gamma_i}^{(\lambda)}$ ($\vec{L}^{(\ell)}$) for even λ are even under time reversal, while the functions with odd λ are odd under time inversion.

Application of the general formulation is made to the various common symmetry types for vibrational-rotational levels occurring for molecules with T_d symmetry. In particular for $\ell=0$ (representing the ground state or a non-degenerate vibrational state with either A_1 or A_2 symmetry (i.e. the ν_1 vibrational state of methane which has A_1 symmetry), then the only basis matrix which enters Eq. (3) is $j_{A_1}^{(0)}(L^{(0)}) = 1$. Thus the sum over symmetries is restricted to those combinations of $j_{A_1}^{(\mu-2\nu)}(\vec{J})$ having A_1 symmetry. Time inversion invariance further restricts the sum to μ = even integer which is written as 2m. Thus the most general rotation Hamiltonian for a non-degenerate level is[9,10]

$$\mathcal{H}_{00}^{(2n)}(\vec{J}) = \sum_{m=0}^{n} \sum_{\nu=0}^{m} a_{A_1}^{(00)}(2m,0,\nu) \, [j(j+1)]^{\nu} \, j_{A_1}^{(2(m-\nu))}(\vec{J}). \quad (6)$$

Table 1 gives the number of $a_{A_1}^{(\ell)}(\mu,\lambda,\nu)$ coefficients which occur in Eq. (3) for ℓ values in the range $0 \leqslant \ell \leqslant 3$, $0 \leqslant \nu \leqslant 10$ and all allowed values of λ,ν. In particular, for $\ell=0$, then λ is restricted to $\lambda=0$, and ν is restricted to $0 \leqslant \nu \leqslant m$. Table 1 then gives one non-vanishing term for m=0 (namely with coefficient $a_{A_1}^{(00)}(0,0,0)$, and one non-vanishing term for m=1 (namely with coefficient $a_{A_1}^{(00)}(2,0,1)$), since the symmetry type A_1 does not occur for $\lambda=2$. Table 1 shows that for m=2 there are two non-vanishing terms in Eq. (6), and these correspond to coefficients $a_{A_1}^{(0,0)}(4,0,0)$ and $a_{A_1}^{(0,0)}(4,0,2)$. The rotational Hamiltonian $\mathcal{H}_{00}^{(2n)}(\vec{J})$ obtained from Eq. (6) has precisely the same form as the Hamiltonian used previously by other workers.[9,10]

The next important application of Eq. (3) to the vibrational-rotational spectrum for methane is to the ν_3 and ν_4 levels which have F_2 symmetry[7] and are 3-fold degenerate ($\ell=1$). The Hamiltonian for $\ell=1$ can be written for levels with either F_1 or F_2 symmetry as:[11]

$$\mathcal{H}_{11}^{(2n)}(\vec{J}) = \sum_{m=0}^{n} \sum_{\nu=0}^{m} a_{A_1}^{(11)}(2m,0,\nu)[j(j+1)]^{\nu} \{j_{A_1}^{(0)}(\vec{L}^{(1)}), j_{A_1}^{(2(m-\nu))}(\vec{J})\}_{A_1}$$

$$+ \sum_{m=0}^{n-1} \sum_{\nu=0}^{m} a_{F_1}^{(11)}(2m+1,1,\nu)[j(j+1)]^{\nu} \{j_{F_1}^{(1)}(\vec{L}^{(1)}), j_{F_1}^{(2(m-\nu)+1)}(\vec{J})\}_{A_1}$$

$$+ \sum_{m=1}^{n} \sum_{\nu=0}^{m-1} a_{E}^{(11)}(2m,2,\nu)[j(j+1)]^{\nu} \{j_{E}^{(2)}(\vec{L}^{(1)}), j_{E}^{(2(m-\nu))}(\vec{J})\}_{A_1}$$

$$\sum_{m=1}^{n} \sum_{\nu=0}^{m-1} a_{F_2}^{(11)}(2m,2,\nu)[j(j+1)]^{\nu} \{j_{F_2}^{(2)}(\vec{L}^{(1)}), j_{F_2}^{(2(m-\nu))}(\vec{J})\}_{A_1} \qquad (7)$$

in which the sum on λ in Eq. (3) has been written explicitly. The first sum, corresponding to $\lambda=0$, is identical to the Hamiltonian in Eq. (6), except that $j_{A_1}^{(0)}(\vec{L}^{(1)})$ is a (3x3) unit matrix, while $j_{A_1}^{(0)}(\vec{L}^{(0)})$ is the scalar 1. The second term in Eq. (7) is for $\lambda=1$, and time reversal symmetry restricts the sum to odd powers of $\vec{J}$ as indicated since only $\Gamma_i = F_1$ symmetry occurs for $j_{\Gamma_i}^{(1)}(\vec{L}^{(1)})$. To obtain a scalar product with A_1 symmetry, the basis function $j_{\Gamma_i}^{(\mu-2\nu)}(\vec{J})$ must have $\Gamma_i = F_1$. The number of coefficients occurring for each order m is found in Table 1 for $\ell=1$ and F_1 symmetry. Similary for $\lambda=2$, two symmetry types occur, namely E and F_2 and time reversal symmetry requires even powers of $\vec{J}$ in the last two sums in Eq. (7). The number of expansion coefficients is again found from Table 1 using the entries listed under $\ell=1$, and E and F_2 symmetries, respectively. The Hamiltonian in Eq. (7) is identical to that used by Robiette et al.[11,12]

To treat the ν_2 level in methane, it is necessary to write Eq. (3) for $\ell=2$ which is appropriate for treating the coupled E and F_2 vibrational modes. An isolated E mode can be treated by the introduction of the 4 basis matrices $j_{\Gamma_i}^{(\beta)}(d_e)$ having ExE = $A_1 + A_2 + E$ symmetry and given by

$$j_{A_1}^{(0)}(d_e) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \qquad j_{A_2}^{(1)}(d_e) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

$$j_{E}^{(2)}(d_e) = \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix}, \qquad \text{and} \quad j_{E*}^{(2)}(d_e) = \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} \tag{8}$$

where the β index is used as a convenient label to indicate time inversion and d_e refers to the part of the d-function that has E symmetry. The resulting Hamiltonian appropriate to the ν_2 vibrational state of methane can then be written as[11]

$$\mathcal{H}_{ee}^{(2n)}(\vec{J}) = \sum_{m=0}^{n} \sum_{\nu=0}^{m} a_{A_1}^{(ee)}(2m,0,\nu)[j(j+1)]^{\nu} \{j_{A_1}^{(0)}(d_e),\ j_{A_1}^{(2(m-\nu))}(\vec{J})\}_{A_1}$$

$$+ \sum_{m=1}^{n} \sum_{\nu=0}^{m} a_{A_2}^{(ee)}(2m+1,1,\nu)[j(j+1)]^{\nu}\{j_{A_2}^{(1)}(d_e),\ j_{A_2}^{(2(m-\nu)+1)}(J)\}_{A_1}$$

$$+ \sum_{m=1}^{n} \sum_{\nu=0}^{m} a_{E}^{(ee)}(2m,2,\nu)[j(j+1)]^{\nu}\{j_{E}^{(2)}(d_e),\ j_{E}^{(2(m-\nu))}(\vec{J})\}_{A_1}$$

$$\tag{9}$$

in which the proper linear combination of operators J has been taken to preserve time inversion symmetry. The number of coefficients $a_{\Gamma_k}^{(ee)}(\mu,\beta,\nu)$ corresponding to each value of μ is listed in Table 2 under $\Gamma_i = E$, $\Gamma_j = E$ and $\Gamma_k = A_1$, A_2 or E. Further discussion of this table is given below. The Hamiltonian given by Eq. (9) has also been used previously to treat the ν_2 level of methane.[10]

The present work makes it possible to simultaneously derive the coupling between degenerate and nearly degenerate vibrational levels to various orders

in $\vec{J}$. The general formulation for this coupling is given below in the context of the coupling between an E and an F_2 (or F_1) vibrational level. This particular coupling block is important for the methane molecule and is present in the Hamiltonian $\mathcal{H}_{22}^{(2n)}(\vec{J})$ for $\ell = 2$, which contains the block $\mathcal{H}_{ee}^{(2n)}(\vec{J})$ given by Eq. (9). In Section III is presented a perturbation approach that reduces the number of expansion coefficients that must be used to yield energy eigenvalues for a given order in the expansion.

The full expansion for $\ell=2$ in T_d symmetry reduces to coupled E and F_2 (or E and F_1) vibrational states. The Hamiltonian for $\ell=2$ is then written as:[11]

$$
\mathcal{H}_{22}^{(2n)}(\vec{J}) = \begin{pmatrix} \mathcal{H}_{ee}^{(2n)}(\vec{J}) & \mathcal{H}_{ef}^{(2n)}(\vec{J}) \\ \\ \mathcal{H}_{ef}^{(2n)}(\vec{J})^{\dagger} & \mathcal{H}_{ff}^{(2n)}(\vec{J}) \end{pmatrix} \tag{10}
$$

where the diagonal blocks are given by Eq. (9) for $\mathcal{H}_{ee}$ and Eq. (9) for $\mathcal{H}_{ff} = \mathcal{H}_{11}$. The diagonal blocks yield energies for uncoupled ν_2 and ν_4 levels for methane. Since these levels are nearly degenerate, they are strongly coupled, and this coupling is treated by the off-diagonal blocks $\mathcal{H}_{ef}^{(2n)}(\vec{J})$. The symmetry and functional form for these coupling blocks are found by expanding the general Hamiltonian in Eq. (3) and then identifying the resulting off-diagonal blocks with $\mathcal{H}_{ef}^{(2n)}(\vec{J})$. In this expansion the basis matrices $\vec{L}^{(2)}$ are 5 x 5 matrices appropriate to $\ell = 2$. The number of expansion coefficients for each value of μ (i.e. J^{μ}) is found in Table 2 under $\Gamma_i = E$, $\Gamma_j = F_2$. In this table blocks with the same symmetry are coupled for $\mu = 0$ (i.e. J^0) and these terms are called Fermi coupling terms.[2] the coupling of two different blocks by terms linear in $\vec{J}$ are called Coriolis coupling

terms.[2] Terms in the coupling block $\mathcal{H}_{ef}^{(2n)}(\vec{J})$ corresponding to $\mu \geq 2$ have no special designations, as do the terms corresponding to $\mu = 0,1$. From Table 2 it is seen that Eq. (10) has no Fermi coupling terms and 1 Coriolis coupling term. Table 2 also gives the number of terms which occur in the coupling blocks for each μ in the range $2 \leq \mu \leq 10$. Also included in Table 2 is the number of expansion coefficients associated with general coupling blocks of Γ_i and Γ_j symmetries; such coupling blocks occur in Hamiltonians $\mathcal{H}_{\ell\ell}^{(2n)}(\vec{J})$ for $\ell > 2$.

The rotational Hamiltonians $\mathcal{H}_{oo}^{(2n)}(\vec{J})$, $\mathcal{H}_{11}^{(2n)}(\vec{J})$ and $\mathcal{H}_{ee}^{(2n)}(\vec{J})$ presented in this section have all been used to fit the rotational levels for the vibration states in the methane molecule. The total number of coefficients which is required for the $2n^{th}$ order phenomenological Hamiltonian is given in the first 3 lines of Table 3. Thus we see that for the uncoupled ν_1, ν_2, ν_3, and ν_4 levels the 8th order Hamiltonians have 11,26,48 and 48 expansion coefficients respectively. The applications of phenomenological Hamiltonians that have previously been made to methane have not been able to fit the experimentally measured levels over the full range of j quantum numbers that are experimentally accessible.[12] Various schemes have been proposed to improve the agreement between the experimental data and the phenomenological Hamiltonians, and these schemes have generally involved inclusion of coupling terms between nearly degenerate vibrational states. The number of coefficients listed for the coupled vibrational levels on the last 3 lines of Table 3 assumes that the coupling terms are included to the same order in J as in the diagonal blocks. In application of these equations to a physical problem, the magnitudes of the coupling parameters are such that they often can be treated in perturbation theory following the formulation given here. In addition, a somewhat different type of perturbation theory, based on

approximate spherical symmetry for the molecule (a jellium approximation for the unperturbed molecule), can be useful in certain physical situations. This type of perturbation approach is presented in the next section.

III. Jellium Perturbation Model

The formulation of the phenomenological Hamiltonian in Section II, though mathematically correct, is often inconvenient to apply because of the large number of coefficients $a_{\Gamma_i}^{(\ell\ell)}(\mu,\lambda,\nu)$ that must be determined from experiment. In this section, a perturbation theory approach is presented which yields a more convenient form of the phenomenological Hamiltonian specific to a given molecule. In this formulation, a jellium model with spherical symmetry is assumed for the zeroth order Hamiltonian, and the specific symmetry is introduced by a perturbation term with the proper symmetry. For example, the perturbation theory for a molecule with T_d symmetry would be written as

$$\tilde{\mathcal{H}}_{\ell\ell}^{(2n)} = [\mathcal{H}_{\ell\ell}^{(2n)}]_\sigma + [\mathcal{H}_{\ell\ell}^{(n)}]'_{T_d} \tag{11}$$

in which the unperturbed zeroth order Hamiltonian has full rotational symmetry and is written as $[\mathcal{H}_{\ell\ell}^{(2n)}]_\sigma$ and the perturbation Hamiltonian is written as $[\mathcal{H}_{\ell\ell}^{(n)}]'_{T_d}$. A discussion of each term in Eq. (11) is now presented.

The assumption of spherical symmetry for $[\mathcal{H}_{\ell\ell}^{(2n)}]_\sigma$ implies that all expansion parameters $a_{\Gamma_i}^{\ell\ell}(\mu,\lambda,\nu)$ in Eq. (3) for a given order μ are equal, independent of symmetry type Γ_i, so that the expansion parameters for the unperturbed term are written as

$$[a_{\Gamma_i}^{(\ell\ell)}(\mu,\lambda,\nu)]_\sigma \equiv \delta_{\lambda,\mu-2\nu}\ \sigma_\lambda^{(\ell\ell)}(\nu) \tag{12}$$

This assumption and Eq. (3) enables one to write the unperturbed Hamiltonian as

$$[\mathcal{H}_{\ell\ell}^{(2n)}(\vec{J})]_\sigma = \sum_{\lambda=0}^{2\ell} \sum_{\nu=0}^{\{n-\frac{\lambda}{2}\}} \sigma_\lambda^{(\ell\ell)}(\nu) \, [j(j+1)]^\nu \, \mathcal{P}_\lambda(\vec{L}^{(\ell)} \cdot \vec{J}) \tag{13}$$

in which $\mathcal{P}_\lambda(\vec{L}^{(\ell)} \cdot \vec{J})$ is defined by

$$\mathcal{P}_\lambda(\vec{L}^{(\ell)} \cdot \vec{J}) = \sum_{\Gamma_i} \{j_{\Gamma_i}^{(\lambda)}(\vec{L}^{(\ell)}), \, j_{\Gamma_i}^{(\lambda)'}(\vec{J})\}_{A_1} \, . \tag{14}$$

Using the properties of spherical harmonics, the sum in Eq. (14) can be carried out to give

$$\mathcal{P}_\lambda(\vec{L}^{(\ell)} \cdot \vec{J}) = [\ell(\ell+1)j(j+1)]^{\lambda/2} \, P_\lambda\left(\frac{\vec{L}^{(\ell)} \cdot \vec{J}}{[\ell(\ell+1)j(j+1)]^{1/2}}\right) \tag{15}$$

where $P_\lambda(z)$ is the Legendre polynomial of order λ. We further note that when $\vec{L}^{(\ell)} = \vec{J}$ in Eq. (15), the function $\mathcal{P}_\lambda(\vec{L}^{(\ell)} \cdot \vec{J})$ reduces to $(\vec{J} \cdot \vec{J})^\lambda$, consistent with Eq. (5). The jellium approximation thus leads to level orderings and degeneracies appropriate to vector sums of the angular momenta $\vec{L}^{(\ell)} + \vec{J}$ with quantum numbers $j+\ell$, $j+\ell-1,\ldots j-\ell$. The $(2\ell+1) \times (2\ell+1)$ Hamiltonian defined by Eq. (13) has precisely the same block form as the Hamiltonian of Eq. (3) with T_d symmetry, except that the expansion coefficients $a_{\Gamma_i}^{\ell\ell}(\mu,\lambda,\nu)$ are constrained by Eq. (12). In this way, a major reduction in the number of expansion coefficients is achieved. The number of independent coefficients $\sigma_\lambda^{(\ell\ell)}(\nu)$ in Eq. (13) is listed in Table 4 according to index ℓ and order of the Hamiltonian 2n, where $\lambda \leq 2\ell$ and ν is the largest integer less than or equal to $(n-\lambda/2)$. As an example, for $\ell=0$, truncation of the Hamiltonian at J^6 results in four expansion parameters, written as $\sigma_o^{(000)}(\nu)$; $\nu=0,1,2,3$. To obtain off-diagonal blocks in the Hamiltonian with all the distinct symmetry types that occur in T_d symmetry when the perturbation term in Eq. (11) is introduced, the expansion of the jellium Hamiltonian of Eq. (13) must be carried to terms $n \geq \ell$.

Referring again to Eq. (11), the perturbation Hamiltonian $[\mathcal{H}_{\ell\ell}^{(n)}]_{T_d}$ can be written explicitly using Eq. (3) for $0 \leq \mu \leq n$. To yield contributions to the energy of order $2n$, the perturbation Hamiltonian is truncated at order n. Thus, when the perturbation energy is calculated for levels that are split by an interactions with T_d symmetry, the coupling blocks, taken to order J^n on the off-diagonal positions of the Hamiltonian, yield contributions to the block-diagonal terms of order J^{2n}, which is of the same order as the jellium Hamiltonian. The coefficients in the perturbation Hamiltonian are written as $a_{\Gamma_i}^{(\ell\ell)}(\mu;\lambda,\nu)$, and are cataloged by symmetry type Γ_i, in the same way as the $a_{\Gamma_i}^{(\ell\ell)}(\mu,\lambda,\nu)$ coefficients of Eq. (3). The $a_{\Gamma_i}^{(\ell\ell)}$ coefficient however differs from the $a_{\Gamma_i}^{(\ell\ell)}$ coefficients insofar as the $\alpha_{\Gamma_i}^{(\ell\ell)}$ are constrained to yield the spherically symmetric $\sigma_\lambda^{(\ell,\ell)}(\nu)$ when summed over all symmetry types

$$\sum_{\Gamma_i} \alpha_{\Gamma_i}^{(\ell\ell)}(\lambda + 2\nu, \lambda, \nu) = n_r \sigma_\lambda^{(\ell\ell)}(\nu) \qquad (16)$$

where n_r is the number of distinct representations.

The large reduction in the number of expansion coefficients for the coupled vibrations represented by Eq. (11) relative to the general form of Eq. (3) is shown explicitly in Table 5. In particular the $\ell=2$ Hamiltonian appropriate to the coupled ν_2, ν_4 vibrational states in methane can be modelled using Eq. (11) with 39 coefficients to 8th order which is to be contrasted to 114 coefficients for the full T_d symmetry expansion to 8th

The jellium perturbation theory developed in this section gives a major reduction of expansion coefficients, especially for $\ell \geq 2$ as shown in Table 5. These higher angular momentum states are directly applicable to combination and overtone vibrational states in methane as is detailed in the next section.

IV. <u>Proposed Application of Jellium Model to Methane</u>

Based on the perturbation theory developed in the last section, we now proceed to outline an approach to the Hamiltonian for the methane levels which focusses on those groups of states that lie in approximately the same frequency range. An application of the jellium perturbation expansion to the coupled ν_2, ν_4 modes in methane was carried out by Prof. A.G. Robiette using his collected experimental data set for these levels. The results are quoted in the footnote to the table 5. Prof. Robiette achieves somewhat better fits to the experimental data by judicious selection of certain terms in the exact Hamiltonian of Eq. (10).

All the vibrations of the jellium molecule can be approximately specified in terms of the three fundamental vibrations which are specified by $\ell = 0.1$ and 2. The state of the jellium molecule is then denoted by a set of 3 integers $\vec{n}_\ell = (n_0, n_1, n_2)$ which specify how many quanta n_ℓ are present in each of the three ℓ states. When either harmonics and/or combination modes are present, it is necessary to use a vector model to obtain the total vibrational angular momentum quantum number $\mathcal{L}$. The jellium model Hamiltonian is written in terms of $\mathcal{L}$, as are the corresponding energy levels given on the left side of Table 6 and denoted by $\vec{n}_\ell$ and $\mathcal{L}$. We note from Table 6 that in the methane molecule there are a number of accidental near-degeneracies; more specifically many of the vibrations are such that the methane levels occur in approximate multiples of 1450 cm^{-1}, as emphasized by the grouping of levels given in Table 6. Thus the approximate position of the jellium vibrations in methane follow the empirical relations given by

$$\omega_{\mathcal{L}}(\vec{n}_\ell) \simeq 1450 \left[n(n_0 + n_1) + n_2 \right] cm^{-1} \qquad (17)$$

Thus the ground state (000) for $\mathcal{L} = 0$ is isolated, doesn't interact strongly with any other state and remains non-degenerate when the perturbation with T_d symmetry is introduced. The (001) jellium state for $\mathcal{L} = 2$ has 5 degenerate vibrational levels at 1450 cm^{-1} and gives rise to a coupled Hamiltonian having the form of Eq. (13) and this level splits under the T_d perturbation of the form of Eq. (1) into a 3-fold level with F_2 symmetry and a higher lying 2-fold level with E symmetry. The next set of states at about 2900 cm^{-1} consists of the (100) level with $\mathcal{L} = 0$, the (010) 3-fold degenerate level with $\mathcal{L} = 1$ and the (002) level with $\mathcal{L} = 4,2$, and 0. The (002) overtone for $\ell = 2$ would according to the vector model correspond to $\mathcal{L} = 4,3,2,1,0$ but the odd values of $\mathcal{L}$ do not occur because these states are odd under the permutation of identical particles, and phonons are Bose particles. The Hamiltonian for the coupled jellium states with energies near 2900 cm^{-1} is written as

$$[\mathcal{H}_{2900}]_\sigma = \left(H \begin{array}{c} \vec{n}_\ell, \ \vec{n}_{\ell'} \\ \mathcal{L}, \mathcal{L}' \end{array} \right) \tag{18}$$

containing 5 x 5 = 25 blocks[13] which are labelled by the $\vec{n}_\ell$, $\mathcal{L}$ indices listed in Table 5 and enumerated explicitly above. The most important coupling terms are those for $\mathcal{L} = \mathcal{L}'$ (which contains Fermi coupling as the leading term in the expansion) and $\mathcal{L} = \mathcal{L}' \pm 1$ (where the leading term in the expansion represents Coriolis coupling). The introduction of the perturbation with T_d symmetry follows the perturbation theory of Eq. (11). The resulting splitting of the jellium levels on the left hand columns of Table 6 are indicated in the right hand columns of Table 6, in terms of the appropriate irreducible representations of T_d, the number of phonons $\vec{n}_{\nu i}$ with mode frequencies ν_1, ν_2, ν_3 and ν_4 and finally the experimental values of the mode frequencies $^2 \omega_{\Gamma_i}(\vec{n}_{\nu i})$.

The groupings of levels near 4350 cm^{-1} are also indicated in Table 6, together with the jellium model quantum numbers and mode frequencies $\omega_{\mathcal{L}}(\vec{n}_{\ell})$, and also the corresponding level splittings which occur in T_d symmetry.

V. Summary

High symmetry molecules represent a theoretical challenge in molecular physics for two essential reasons: (1) Molecules with cubic symmetry must have at least 4 identical atoms (perhaps more) and hence 6 or more internal vibrational degrees of freedom (i.e. a large number of modes) and (2) symmetry forces some of these modes to be degenerate. The high symmetry furthermore increases the probability for near-degeneracies which further complicate the calculation of the vibrational energies. The models for these molecules must therefore make extensive use of group theoretical techniques.

This paper gives the most general group theoretical form for the rotational Hamiltonian associated with the vibrational states of these high symmetry molecules and the use of this Hamiltonian is illustrated for the methane model. In addition a perturbation theory is developed based on a jellium model for the molecule which enables one to significantly reduce the number of expansion coefficients. The overtone and combination modes in the high symmetry molecules occur in the same frequency region as the fundamental vibrations and perturbation theory developed in this paper is formulated to treat to the coupling between this extended set of nearly degenerate modes in the methane molecule.

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jellium model to the coupled ν_2, ν_4 band in methane using his extensive data set. This work was supported by the Air Force Systems Command through contract # F19628-77-C-0026.

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Table 1 Number of Expansion Coefficients $a_{\Gamma_1}^{(\ell,\ell)}(\mu,\lambda,\nu)$ in

Eq. (3) for all allowed λ and ν in the range $0 \le \lambda \le 2\ell$ and $0 \le \nu \le \mu/2$.

ℓ	Γ	Number of Expansion Coefficients										
		$\mu = 0$	1	2	3	4	5	6	7	8	9	10
0	A_1	1		1		2		3		4		5
1	A_1	1		1		2		3		4		5
	E			1		2		3		5		7
	F_1		1		2		4		6		9	
	F_2			1		2		4		6		9
2	A_1	2		2		4		6		8		10
	A_2				1		1		2		3	
	E			2		4		6		10		14
	F_1		2		4	1	8	2	12	4	18	6
	F_2			2	1	4	2	8	4	12	6	18
3	A_1	3		3		6		9		12		15
	A_2				1		1	1	2	1	3	2
	E			3		6	1	9	2	15	3	21
	F_1		4		8	2	16	4	24	8	36	12
	F_2			4	2	8	4	16	8	24	12	36

Table 2   Number of expansion coefficients associated with the coupling terms in the phenomenological Hamiltonian (a,b)

Γ_i	Γ_j	Symmetry	$\mu=0$	1	2	3	4	5	6	7	8	9	10
A_1 A_2	A_1 A_2	A_1	1		1		2		3		4	1°	5
A_1	A_2	A_2				1		1	1	2	1	3	?
A_1 A_2	E E	E			1		2	1	3	2	5	3	7
A_1 A_2	F_2 F_1	F_2			1	1	2	2	4	4	6	6	9
A_1 A_2	F_1 F_2	F_1		1		2	1	4	2	6	4	9	6
E	E	A_1	1		1		2		3		4	1°	5
		A_2				1		1	1°	2	1°	3	2°
		E			1		2	1°	3	2°	5	3°	7
E	F_1	F_1		1		2	1	4	2	6	4	9	6
E	F_2	F_2			1	1	2	2	4	4	6	6	9
F_1	F_1	A_1	1		1		2		3		4	1°	5
F_2	F_2	E			1		2	1°	3	2°	5	3°	7
		F_1		1		2	1°	4	2°	6	4°	9	6°
		F_2			1	1°	2	2°	4	4°	4	6°	7
F_1	F_2	A_2				1		1	1	2	1	3	2
F_2	F_1	E			1		2	1	3	2	5	3	7
		F_1		1		2	1	4	2	6	4	9	6
		F_2			1	1	2	2	4	4	6	6	9

a) Γ_i and Γ_j denote the symmetries of the coupled terms.

b) The terms which are odd under the time inversion symmetry are labelled with a zero superscript when $\Gamma_i = \Gamma_j$. These terms are not allowed on the diagonal block of the Hamiltonian, i.e. Eqs. (6), (7) and (9) do not contain any terms that are odd under time inversion. However, the off-diagonal interaction that couples two modes of the same symmetry (e.g. the ν_3 and ν_4 vibrational levels in methane) would include the odd terms indicated in this table.

Table 3   Total Number of Independent Expansion Coefficients

$a_{\Gamma_i}^{(\ell\ell)}(\mu,\lambda,\nu)$ in the Phenomenological T_d Rotational

Hamiltonian Summed to $\nu = 2n$

Vibrational Symmetry	Dimension	$2n = 2$	4	6	8	10
		Number of Independent Constants				
A_1 or A_2	1 x 1	2	4	7	11	16
E	2 x 2	3	8	15	26	41
F_1 or $F_2^{a)}$	3 x 3	5	13	27	48	78
(A_1,E) or (A_2,E)	3 x 3	6	15	29	51	81
(A_1,F_2) or (A_2,F_1) (A_1,F_1) or (A_2,F_2)	4 x 4	8	21	44	79	129
(E,F_2) or (E,F_1)	5 x 5	10	29	62	114	189

a) The $2n^{th}$ order rotational Hamiltonian used by various authors for the
ν_3 and ν_4 states in methane includes in addition the A_1 symmetry
combinations with $\mu = 2n + 2$. Hence their 2,4,6,8 and 10th order
Hamiltonians have 7,16,31,53 and 85 parameters respectively.

Table 4   Total Number of Independent Coefficients $\sigma_\lambda^{(\ell\lambda)}(\nu)$ in the Jellium Hamiltonian [a] of Order $2n$

	Total Number of Coefficients for Order $2n$				
ℓ	$2n = 2$	4	6	8	10
0	2	3	4	5	6
1	4	7	10	13	16
2	4	9	14	19	24
3	4	9	16	23	30

[a] The integers λ and ν are constrained by $0 \leqslant \lambda \leqslant 2\ell$ and $0 < \nu < \{n - \lambda/2\}$ in which $\{n - \lambda/2\}$ is the largest integer less than or equal to $n - \lambda/2$.

Table 5   Comparison Between the Total Number of Symmetry Allowed
           Coefficients in the "Full" Phenomenological Hamiltonian
           (Eq. (3)) and in the "Jellium" Perturbation Expansion of
           Eq. (11).

Total Number of Coefficients for Order 2n

ℓ	Type	$3n = 2$	4	6	8	10
0	full	2	4	7	11	16
	jellium	2	3	4	6	7
1	full	5	13	27	48	78
	jellium	4	8	12	19	25
2	full	10	29	62	114	189
	jellium	6	15 a)	24 b)	39	53
3	full	17	50	111	207	347
	jellium	9	22	38	64	90

The weighted standard deviations of the fits to the ν_2, ν_4 levels in methane are

a) 0.0056 cm^{-1} fit to levels through J=12.

b) 0.0205 cm^{-1} fit to levels through J=20.

Table 6   Vibrational mode frequencies for CH$_4$ as suggested by a perturbation expansion based on a spherically symmetric unperturbed state.

mode[a) $\vec{n}_\ell$	Irred. Repr.[b) $\mathcal{L}$	Position(cm^{-1}) $\omega_{\mathcal{L}}(\vec{n}_\ell)$	Irred. Repr. Γ_i	mode[d) $\vec{n}_{\nu_i}$[g)	Position(cm^{-1})[e) $\omega_{\Gamma_i}(\vec{n}_{\nu_i})$
		Spherical Symmetry		T$_d$ Symmetry	
(000)	0	0.0	A$_1$	[0 0 0 0]	0.0
(001)	2	1450	E	[0 1 0 0]	1526.0
			F$_2$	[0 0 0 1]	1306.2
(002)	4	2900	A$_1$ + E	[0 2 0 0]	3071.5
			F$_1$ + F$_2$	[0 1 0 1]	2823.0
	2		E + F$_2$		
	0	2600	A$_1$	[0 0 0 2]	2600.
(100)	0	2900	A$_1$	[1 0 0 0]	2914.2
(010)[f)	1	3000	A$_2$ x (F$_1$)	[0 0 1 0]	3019.5
(003)	6	4470	A$_1$ + A$_2$ + E	[0 3 0 0]	[4578]
			F$_1$ + 2F$_2$	[0 2 0 1]	[4358]
	4		A$_1$+E+F$_1$+F$_2$	[0 1 0 2]	4123
	3		A$_2$+F$_1$+F$_2$		
	2	4020	E + F$_2$	[0 0 0 3]	[3919]
	0		A$_1$		
(101)	2	4300	E	[1 1 0 0]	[4440]
			F$_2$	[1 0 0 1]	4216.3
(011)[f)	3		A$_2$x(A$_2$+F$_1$+F$_2$)	[0 0 1 1]	4313.2
	2	4400	A$_2$x(E + F$_2$)		
	1		A$_2$x(F$_1$)	[0 1 1 0]	4546.0

a) A number representation is used in which the number of vibrational modes for angular momentum ℓ is written as n_ℓ and the set of modes by
$$\vec{n}_\ell = (n_o, n_1, n_2).$$

b) In the overtone modes (i.e. $n_\ell > 1$), not all allowed $\mathcal{L}$ values occur because of the identical nature of the particles (phonons). The functions must be even under the exchange of coordinates of identical particles.

c) This is a rough estimate of the mode position before the application of the T$_d$ perturbation. The indicated accidental degeneracy between the various $\mathcal{L}$'s is not symmetry imposed and should be lifted within the spherical approximation.

d) The mode designation in T_d symmetry indicates the number of ν_i modes by n_{ν_i} and the set of modes by $\vec{n}_{\nu_i} = [n_{\nu_1}, n_{\nu_2}, n_{\nu_3}, n_{\nu_4}]$.

e) The modes positions are experimental measurements of F_2 symmetry modes as listed in Ref. 10 and also estimates based upon the multiples of the fundamental frequencies shown in brackets.

f) The modes involving an odd number of $\ell = 1$ vibrations when taken in T_d symmetry must all be considered as a direct product with A_2.